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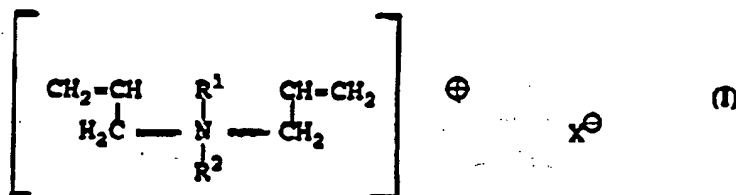
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(21) International Application Number: PCT/US95/15139 (22) International Filing Date: 21 November 1995 (21.11.95) (30) Priority Date: TO94A000991 6 December 1994 (06.12.94) IT (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): PALUMBO, Gianfranco (IT/DE); Georgenfeld 7, D-41348 Bad Homburg (DE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).	(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GR, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).  Published With international search report.	

(54) Title: ABSORBENT MATERIAL

(57) Abstract

The present invention provides a superabsorbent material which comprises a combination of: (1) an anionic superabsorbent in which from 20 to 100 % of the functional groups are in free acid form, and (2) a cationic superabsorbent in which from 20 to 100 % of the functional groups in basic form, the cationic superabsorbent being based on a polysaccharide or a polymer of units of a monomer of formula (I)

wherein R<sup>1</sup> and R<sup>2</sup> which may be the same or different, are each organic radicals which do not adversely affect the properties of the polymer and X is a suitable anion. The combination is particularly effective as a superabsorbent in the case of electrolyte containing solutions such as menses and urine.



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### ABSORBENT MATERIAL

The present invention relates to an absorbent material, more particularly a material of the type commonly referred to as a "superabsorbent".

The substances currently termed "superabsorbents" are typically slightly cross-linked hydrophilic polymers. The polymers may differ in their chemical nature but they share the property of being capable of absorbing and retaining even under moderate pressure amounts of aqueous fluids equivalent to many times their own weight. For example superabsorbents can typically absorb up to 100 times their own weight or even more of distilled water.

Superabsorbents have been suggested for use in many different industrial applications where advantage can be taken of their water absorbing and/or retaining properties and examples include agriculture, the building industry, the production of alkaline batteries and filters. However the primary field of application for superabsorbents is in the production of hygienic and/or sanitary products such as disposable sanitary napkins and disposable diapers either for children or for incontinent adults. In such hygienic and/or sanitary products, superabsorbents are used, generally in combination with cellulose fibres, to absorb body fluids such as menses or urine. However, the absorbent capacity of superabsorbents for body fluids is dramatically lower than for deionised water. It is generally believed that this effect results from the electrolyte content of body fluids and the effect is often referred to as "salt poisoning".

The water absorption and water retention characteristics of superabsorbents are due to the presence in the polymer structure of ionisable functional groups. These groups are

usually carboxyl groups, a high proportion of which are in the salt form when the polymer is dry but which undergo dissociation and solvation upon contact with water. In the dissociated state, the polymer chain will have a series of functional groups attached to it which groups have the same electric charge and thus repel one another. This leads to expansion of the polymer structure which, in turn, permits further absorption of water molecules although this expansion is subject to the constraints provided by the cross-links in the polymer structure which must be sufficient to prevent dissolution of the polymer. It is assumed that the presence of a significant concentration of electrolytes in the water interferes with dissociation of the functional groups and leads to the "salt poisoning" effect. Although most commercial superabsorbents are anionic, it is equally possible to make cationic superabsorbents with the functional groups being, for example, quaternary ammonium groups. Such materials also need to be in salt form to act as superabsorbents and their performance is also affected by the salt-poisoning effect.

Attempts have been made to counteract the salt poisoning effect and improve the performance of superabsorbents in absorbing electrolyte containing liquids such as menses and urine. Thus Japanese Patent Application OPI No. 57-45,057 discloses an absorbent which comprises a mixture of a superabsorbent such as a cross-linked polyacrylate with an ion exchange resin in powder or granular form. EP-A-0210756 relates to an absorbent structure comprising a superabsorbent and an anion exchanger, optionally together with a cation exchanger, wherein both ion exchangers are in fibrous form. Combining a superabsorbent with an ion exchanger attempts to alleviate the salt poisoning effect by using the ion exchanger to reduce the salt content of the liquid. The ion exchanger has no direct effect on the performance of the superabsorbent and it may not be possible to reduce the salt content sufficiently to have the desired effect on the

overall absorption capacity of the combination. In addition, besides being expensive, the ion exchanger has no absorbing effect itself and thus acts as a diluent to the superabsorbent.

5

EP-A-0487975 relates to a cross-linked ampholytic copolymer said to be highly absorbent to aqueous electrolyte solutions and formed from an ampholytic ion pair monomer, a co-monomer and a cross-linking agent. It is assumed that when the ampholytic ion pair monomer is incorporated into the polymer backbone the ion pairs act as ionic cross-links which remain intact in deionised water but are broken in salt solution. Accordingly the copolymer is sensitive to the ionic strength of the solution in the sense that the effective degree of cross-linking is reduced as the ionic strength increases. Whilst this produces an absorbent whose absorption capacity in deionised water and in salt solution more closely approximate to one another, it does not necessarily improve absorption in the presence of salt as the polymer is not able to desalt the ionic solution and thus increase the absorption power.

EP-A-0161762 relates to a water swellable, water insoluble polymer produced by inverse suspension polymerisation of a diallylic ammonium salt monomer, an acrylic monomer and a cross-linking agent. The product is an acrylic acid polymer containing both cationic and anionic groups in the chain which is intended for use as a superabsorbent in salt form. It is claimed that the material can absorb the same quantity of water irrespective of the salt content of the water but absorption is at a low level and the material does not show any significant improvement in its water absorption in the presence of salt as compared to conventional superabsorbents. EP-A-0161763 relates to a similar superabsorbent made by polymerising a diallyl ammonium compound and a cross-linking agent by suspension polymerisation.

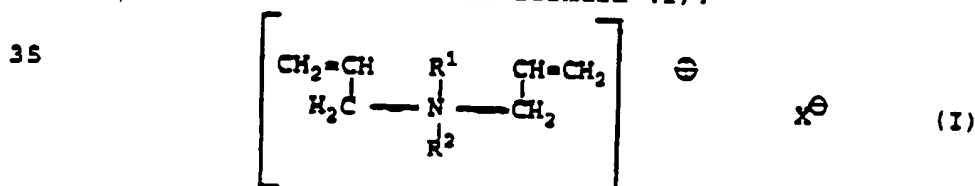
WO 92/20735 relates to a superabsorbent which is said to be substantially tolerant to salt solutions and which comprises a swellable hydrophobic polymer and an ionizable surfactant. The specification also discloses (but does not claim) an alternative embodiment which uses a cationic superabsorbent which exchanges  $\text{Cl}^-$  with  $\text{OH}^-$  and an anionic superabsorbent which exchanges  $\text{Na}^+$  with  $\text{H}^+$ . No working examples of such a system are given and the superabsorbent gels disclosed are generally acrylamide derivatives. Acrylamide derivatives include the amide bond which is subject to hydrolysis at low alkaline pH (about pH 8) with release of toxic hydrolysis products. Hydrolysis problems will be exacerbated if the polymer is prepared and used in base form. An alkaline pH of about 8 may well arise in baby urine if fermentation of urea to ammonia takes place so that tissue hydrolysis products would be liable to be formed from acrylamide derivatives in contact with urine at this pH.

An object of the present invention is to provide a superabsorbent with improved performance in the presence of electrolyte, for example in the case of menses or urine.

The present invention provides a superabsorbent material which comprises a combination of

(1) an anionic superabsorbent in which from 20 to 100% of the functional groups are in free acid form; and

(2) a cationic superabsorbent in which from 20 to 100% of the functional groups are in basic form, the cationic superabsorbent being based on a polysaccharide or a polymer of units of a monomer of formula (I):



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wherein  $R^1$  and  $R^2$ , which may be the same or different, are each organic radicals which do not adversely affect the properties of the polymer and X is a suitable anion.

5 The anionic superabsorbent preferably has 50 to 100% and more preferably has substantially 100% of the functional groups in free acid form. The cationic superabsorbent preferably has 50 to 100% and more preferably has substantially 100% of the functional groups in basic form.

10 As already noted above, both anionic and cationic superabsorbents have to have functional groups in salt form before they act as superabsorbents. Commercially available superabsorbents are usually available in salt form. It has  
15 now surprisingly been found according to the present invention that a combination of an anionic superabsorbent in free acid form with a cationic superabsorbent as defined above in basic form is particularly effective as a superabsorbent in the case of electrolyte containing  
20 solutions, for example menses and urine.

Whilst not wishing to be bound by any particular theory, it is believed that there is a two fold effect when the superabsorbent material according to the invention is  
25 contacted with an electrolyte containing solution as follows:  
(1) the anionic and the cationic superabsorbent are both converted from a non-absorbing form into the salt forms in which they act as superabsorbents; and  
(2) conversion of the anionic and the cationic  
30 superabsorbent into the salt forms has a de-ionising effect on the solution.

In general the anionic superabsorbent does not behave as an ion exchanger in the sense that contacting the material  
35 alone in acid form with an electrolyte containing solution does not result in conversion to the salt form. The functional groups in anionic superabsorbents are typically

carboxyl groups which act as a weak acid which does not dissociate when placed, for example, in a sodium chloride solution. However, presence of the cationic superabsorbent has the effect of attaching chloride ions from sodium chloride solution, thereby displacing the equilibrium in favour of conversion of the anionic superabsorbent into the salt form.

This conversion of both the anionic and the cationic superabsorbent into the salt form on contact with an electrolyte containing solution has a significant desalting effect on the solution thereby improving the performance of the superabsorbent by alleviating the salt-poisoning effect. In contrast with the use of an ion-exchange resin to desalt the solution (see Japanese Patent Application OPI No. 57-45057 and EP-A-0210756 referred to above) the material having the de-salting effect is the superabsorbent itself. This allows a much greater de-salting effect to be achieved and the material which brings about the de-salting effect does not act as a diluent for the superabsorbent.

The anionic superabsorbent can be any material having superabsorbent properties in which the functional groups are anionic, namely sulphonic groups, sulphate groups, phosphate groups or carboxyl groups. Preferably the functional groups are carboxyl groups. Generally the functional groups are attached to a slightly cross-linked acrylic base polymer. For example, the base polymer may be a polyacrylamide, polyvinyl alcohol, ethylene maleic anhydride copolymer, polyvinylether, polyvinyl sulphonic acid, polyacrylic acid, polyvinylpyrrolidone and polyvinylmorpholine. Copolymers of these monomers can also be used. Starch and cellulose based polymers can also be used including hydroxypropyl cellulose, carboxymethyl cellulose and acrylic grafted starches. Particular base polymers include cross-linked polyacrylates, hydrolysed acrylonitrile grafted starch, starch polyacrylates, and isobutylene maleic anhydride copolymers.



Particularly preferred base polymers are starch polyacrylates and cross-linked polyacrylates.

The functional groups will generally be carboxyl groups.

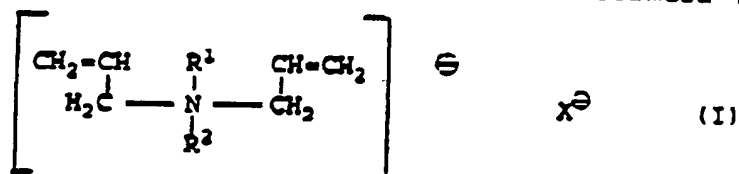
5 Many anionic superabsorbents are available commercially, for example Dow 2090 (Dow), Favor 922 (Stockhausen), Sanwat IM 1500 (Sanyo), Aqualon AQV D3236 (Aqualon Company). Commercially available anionic superabsorbents are generally  
10 sold in salt form and need to be converted to the free acid form for use according to the invention, for example, Favor 922 may be swelled in water, acidified with HCl (0.01M), washed with water to remove excess HCl and dried in an air ventilated oven to obtain Favor 922 in acid form (FAVOR H) as  
15 follows:

Preparation of Favor H

10g of Favor 922 were placed in a 1 litre beaker, and swelled with 500 ml of distilled water under continuous stirring with  
20 a magnetic stirrer. 250 ml of HCl 0.01 M were thereafter added under continuous stirring, and after 30 minutes the gel was filtered with a nonwoven fabric filter. The acidification and filtration steps were repeated until there were no longer any sodium ions present in the washing waters  
25 (the sodium ion content may be determined by a potentiometric method using a selective sodium sensitive electrode). Finally the gel was washed with distilled water to remove the excess acid and the gel was dried in an air ventilated oven at 60°C for 10 hours. The dried polymer obtained was called  
30 Favor H.

Alternatively the anionic superabsorbent may be directly synthesized in acid form by the radical polymerization of the acrylic acid monomer with a crosslinking agent, namely in the  
35 same manner as commercially available superabsorbents are synthesized.

The cationic superabsorbent can also be a materia  
 formed from a polysaccharide based polymer as described above  
 for the anionic superabsorbent but with cationic functional  
 groups. Alternatively the cationic superabsorbent may be  
 based on a polymer of units of a monomer of formula (I):



wherein  $\text{R}^1$  and  $\text{R}^2$  which may be the same or different, are  
 each organic radicals which do not adversely affect the  
 properties of the polymer and X is a suitable anion.

Preferably  $\text{R}^1$  and  $\text{R}^2$  are each independently an  
 optionally substituted saturated hydrocarbon group or aryl  
 group. For example the saturated hydrocarbon group may be an  
 alkyl group which may be straight or branched chain or  
 cyclic. The aryl group also includes arylalkyl groups.  
 Preferably the groups  $\text{R}^1$  and  $\text{R}^2$  have from 1 to 20 carbon  
 atoms, more preferably from 1 to 6 carbon atoms. The  
 saturated hydrocarbon groups or the aryl groups may be  
 substituted by one or more suitable substituents selected  
 from carboxyl, ester, hydroxyl, ether, sulphate, sulphonate,  
 primary, secondary or tertiary amines or quaternary ammonium  
 groups. In this case of ester ( $-\text{CO}_2\text{R}$ ) and ether ( $-\text{O}-\text{R}$ ) the  
 R group is a hydrocarbon radical having from 1 to 20,  
 preferably from 1 to 6 carbon atoms, more preferably the R  
 group is methyl. In the case of aryl groups, suitable  
 substituents include saturated hydrocarbon groups as defined  
 above. The preferred groups for  $\text{R}^1$  and  $\text{R}^2$  are methyl groups.

X may be any suitable anion which may be inorganic or  
 organic. Suitable inorganic anions include halide (in  
 particular fluoride, chloride, bromide and iodide), nitrate,  
 phosphate, nitrite, carbonate, bicarbonate, borate, sulphate

and hydroxide. Suitable organic anions include carboxylate such as acetate, citrate, salicylate and propionate. Preferably the anion is a chloride or hydroxide ion.

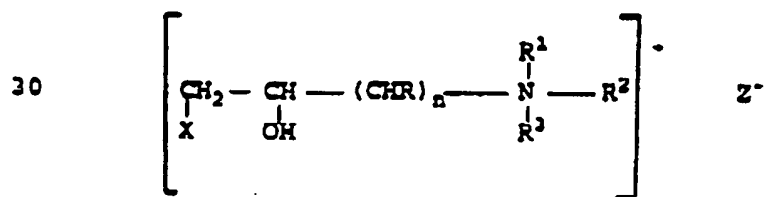
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Preferred monomers are diallyl dimethyl ammonium chloride and dimethyl diallyl ammonium hydroxide.

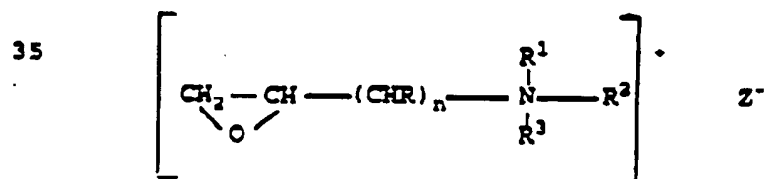
The cationic superabsorbents used according to the present inventions are resistant to hydrolysis at low alkaline pH and thus are not subject to the problems with release of toxic hydrolysis products referred to above in the context of the acrylamide derivatives suggested by WO 92/20735. Examples of suitable cationic functional groups include primary, secondary or tertiary amine groups or quaternary ammonium groups which should be present in base form. Preferably quaternary ammonium groups are used. Preferred base polymers include polysaccharides and polymers based on dimethyldiallyl ammonium chloride.

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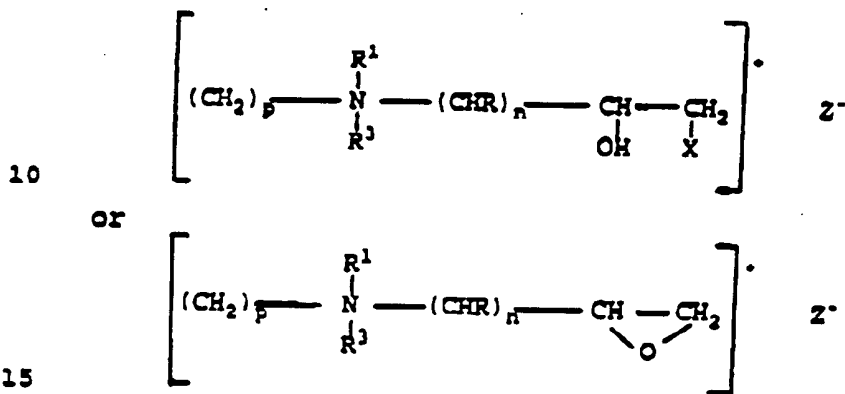
According to one embodiment, the cationic superabsorbent can be a polysaccharide superabsorbent obtained by reacting a fibrous polysaccharide such as cellulose with an excess of a quaternary ammonium compound containing at least one group capable of reacting with polysaccharide hydroxyl groups and having a degree of substitution of 0.5 to 1.1. The quaternary ammonium compound may have the general formula:



or



where n is an integer from 1 to 16; X is halogen; Z is an anion such as halide or hydroxyl; and R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, which may be the same or different, are each hydrogen, alkyl, hydroxyalkyl, alkenyl or aryl and R<sup>2</sup> may additionally represent a residue of formula



where p is an integer from 2 to 10 and n, R, R<sup>1</sup>, R<sup>3</sup>, X and Z have the meanings already defined. Cationic polysaccharide superabsorbents of this type are described in more detail in WO92/19652.

According to another embodiment the cationic superabsorbent may be a cross-linked cellulose based superabsorbent, in particular a cationic polysaccharide, for example a fibrous polysaccharide, having superabsorbent characteristics, the polysaccharide being substituted by quaternary ammonium groups and having a ds of at least 0.5 and the polysaccharide being cross-linked to a sufficient extent that it remains insoluble in water. Superabsorbents of this type are described in more detail in our co-pending patent application No. .... (internal reference DR44).

According to a further embodiment the cationic superabsorbent may be a water-swellaable, water-insoluble polymer comprising units derived from a diallylic quaternary ammonium salt monomer, cross-linked by a suitable polyfunctional vinyl compound, characterised in that the

polymer has been produced by cationic polymerisation in an aqueous phase using a free radical catalyst. Superabsorbents of this type are described in more detail in our co-pending patent application No. .... (internal reference DR43).

5

Preferably the functional groups on anionic superabsorbent are such that the superabsorbent is a weak acid and those on the cationic superabsorbent are such that the superabsorbent is a strong base.

10

In general the ratio of anionic to cationic superabsorbent is in the range 3:1 to 1:5 based on monomer units, more preferably 2:1 to 1:2, each monomer unit having one functional group therein. Most preferably the anionic and cationic superabsorbents are used such that they have equal exchange power so that pH extremes in the bodily fluids absorbed are not reached and the optimum desalting effect is achieved. Cationic and anionic exchange power of the superabsorbent may be experimentally determined by, for example, titration, or in the case of synthetic polymers by a theoretical calculation.

20

The absorbent material according to the invention is particularly suitable for use in applications where it is desired to absorb electrolyte containing aqueous liquids. Examples of such liquids include in particular menses and urine and the absorbent material can be used as the filling in catamenials and diapers generally in admixture with a fibrous absorbent such as cellulose fluff. For this purpose the absorbent according to the invention can be present as granules or fibres.

25

30

The absorbent materials according to the invention show particularly good absorption of electrolyte containing aqueous liquids as is demonstrated below in the following examples by tests carried out using saline solution (1% NaCl) and synthetic urine.

35

Preparation - Cationic Superabsorbent based on  
Dimethyldiallylammonium chloride

CATIONIC POLYMER IN ACID FORM

- 5 219 grams of a 60% aqueous solution of dimethyldiallylammonium chloride (DMAC) available from Fluka were weighed into a 500ml flask. 0.4597 g of bisacrylamide (crosslinker agent) were weighed separately into a 5 ml test tube and was dissolved using 2 ml distilled water. 0.12 g of ammonium persulfate (radical initiator) were dissolved separately in a 5 ml test tube in 2 ml distilled water. The air was removed from the monomer solution by means of a vacuum pump.
- 10
- Under continuous stirring, using a magnetic stirrer, the crosslinker solution and the radical initiator solution were added to the monomer solution, the temperature was adjusted to 60°C by placing the flask in a thermostatic bath for four hours.
- 15
- 20 The solid product formed was cut using a spatula and transferred in a 5 litre beaker containing 4 litres of distilled water, after two hours the swelled gel which had formed was filtered by a nonwoven tissue fabric filter. The gel was dried in a ventilated oven at 60°C for 12 hours.
- 25 100g of a dried polymer called Fai 9 Cl<sup>-</sup> were collected.

Cationic polymer in basic form

- 20 g Fai 9 Cl polymer were placed in a 10 litre beaker and swelled under continuous stirring by adding 4 L of distilled water. After the polymer had swelled 500 ml of 0.01 M NaOH solution were added and after 30 minutes the gel was filtered using a nonwoven fabric tissue filter. These operations (alkalinization and filtering) were repeated until there were no chloride ions in the washing waters (chloride ions may be checked by AgNO<sub>3</sub> reaction).
- 30
- 35

At this point the gel was washed with distilled water until no further evidence of the basic reaction was found in the washing waters. The gel was dried in an air ventilated oven at 60°C for 12 hours. 12 g of polymer were collected and it  
5 was called Fai 9 OH.

### Examples

#### Preparation - Anionic polymer in acid form

10

10 g of superabsorbent polymer Favor 922 (available from Stockhausen) were placed in a 2 litre beaker, and swelled with 500 ml of distilled water under continuous stirring (magnetic stirrer) for 1 hour.

15

500 ml of 0.01 M HCl was added and stirred continuously for 1 hour.

20

The gel was filtered in a nonwoven fabric tissue filter, the step of acidification and filtering of the gel containing solution was repeated until the disappearance of sodium ions from the washing waters (sodium ion content of the solution can be measured by potentiometric method using a sodium sensitive electrode).

25

Finally the gel was washed with distilled water until the washing waters were neutral; the gel was dried in a ventilated oven for 10 hours at 70°C to give 5.5 g of a dried product which was called Favor H<sup>+</sup>.

30

#### 2. Comparative Tests of Liquid Absorption

The test is to demonstrate that the use of both an anionic AGM in acid form and a cationic AGM in base form, when in contact with an aqueous saline solution, act as anionic and  
35 cationic ion exchange resins and cause deionization of the solution. The AGMs are converted in the salt form with improved absorbency due to the reduced salt content of the

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solution.

5 0.2 g of Favor H ( $0.2 \times 1000/72 = 2.78$  mmoles) and 0.4 g of  
Fai 9 OH ( $0.4 \times 1000/143 = 2.80$  mmoles) are weighed into a  
250 ml beaker. Under continuous stirring NaCl it solution is  
dropped into the beaker, the addition is stopped when the gel  
formed is unable to absorb further solution. A minimum time  
of two hours is allowed to elapse.

10 The gel is transferred in a tea-bag type envelope and is  
suspended for 10 min to remove unabsorbed water after which  
the envelope is weighed. Absorbency is measured as follows:

$$A = (W_{wet} - W_{dry}) / (G_1 + G_2)$$

15

where:

A = absorbency in g/g  
W<sub>wet</sub> = weight of the envelope containing the wet AGMs in  
20 g  
W<sub>dry</sub> = weight of the envelope containing the dry AGMs in  
g  
G<sub>1</sub> = weight of the dry anionic AGM in g  
G<sub>2</sub> = weight of the dry cationic AGM in g

25

Absorbency after centrifugation ("retention") is measured by  
placing the tea-bag envelope in a centrifuge for 10 min at 60  
x g after which the envelope is weighed.

30 Retention is measured as follows:

$$R = (W'_{wet} - W_{dry}) / (G_1 + G_2)$$

where:

35

R = absorbency after centrifugation at 60 x g in g/g  
W'<sub>wet</sub> = weight of the envelope containing the wet AGM



15

after centrifugation in g  
Wdry, G1 and G2 are as defined above.

Each of samples A to D were put into a saline solution (1%)  
or solution of synthetic urine and into deionized water.

Sample E was tested only in saline/synthetic urine.

Results are as follows:

	Water Retention g/g	
	Deionised Water	1% NaCl Solution
A-FAVOR (H <sup>+</sup> )	30	3
B-FAVOR (Na <sup>+</sup> )	400	40
C-Fai 9 (OH)	300	45
D-Fai 9 (Cl <sup>-</sup> )	290	44
E-1/3 FAVOR (H <sup>+</sup> ) + 2/3 Fai (OH <sup>-</sup> ) <sup>1)</sup>	-	56

<sup>1)</sup> 1 part by weight Favor H<sup>+</sup> is mixed with two parts by  
weight Fai 9 OH<sup>-</sup> in order to obtain an equimolar mixture of  
the two polymers.

The above results show that the anionic superabsorbents  
in acid form (FAVOR H<sup>+</sup>) shows very little absorption by  
itself in 1% NaCl solution. However in combination with the  
cationic superabsorbent in base form (Fai 9 OH), the material  
shows significantly increased absorption over either FAVOR  
Na<sup>+</sup> or Fai 9 Cl<sup>-</sup>.

It should be noted that the theoretical retention to be  
expected of 1/3 FAVOR H<sup>+</sup> + 2/3 Fai 9 OH is about 31 g/g  
whereas the theoretical retention of 1/3 FAVOR Na<sup>+</sup> + 2/3 Fai  
9 Cl<sup>-</sup> is about 43 g/g. The actual measured amount of 56 g/g  
for 1/3 FAVOR H<sup>+</sup> + 2/3 Fai 9 OH is equivalent to the result

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to be expected of  $1/3$  FAVOR  $\text{Na}^+$  +  $2/3$  Fai 9  $\text{Cl}^-$  in 0.4% NaC and 0.4% NaCl corresponds to the desalting effect that would be obtained by treating 1% NaCl with the mixture of FAVOR H + Fai 9 OH.

5

It should also be noted that 1% NaCl represents a stringent test of the superabsorbent. Studies in the literature show that the salt content of urine varies depending on a number of factors but 1% by weight represents the maximum likely to be encountered in practice.

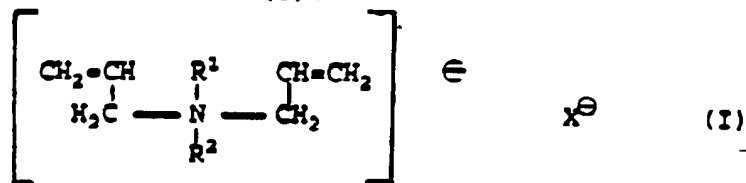
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CLAIMS

1. A superabsorbent material which comprises a combination of

5 (1) an anionic superabsorbent in which from 20 to 100% of the functional groups are in free acid form; and

(2) a cationic superabsorbent in which from 20 to 100% of the functional groups are in basic form, the cationic superabsorbent being based on a polysaccharide or a polymer of a monomer of formula (I):



15 wherein  $\text{R}^1$  and  $\text{R}^2$ , which may be the same or different, are each organic radicals which do not adversely affect the properties of the polymer and X is a suitable anion.

20 2. A superabsorbent material as claimed in claim 1 wherein the anionic superabsorbent has from 50 to 100% of the functional groups in free acid form and wherein the cationic superabsorbent has from 50 to 100% of the functional groups in basic form.

25 3. A superabsorbent material as claimed in claim 1 or 2 wherein the functional groups of the anionic superabsorbent are sulphonic, sulphate, phosphate or carboxyl groups, preferably carboxyl groups.

30 4. A superabsorbent material as claimed in claim 3 wherein the functional groups are attached to a polyacrylamide, polyvinyl alcohol, ethylene maleic anhydride copolymer, polyvinylether, polyvinyl sulphonic acid, polyacrylic acid, 35 polyvinylpyrrolidone, polyvinylmorpholine or copolymers thereof or a starch or cellulose based polymers as base polymer.

5. A superabsorbent material as claimed in claim 4 wherein the starch or cellulose based polymer is hydroxypropyl cellulose, carboxymethyl cellulose or an acrylic grafted starch.

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6. A superabsorbent material as claimed in claim 4 or wherein the base polymer is a cross-linked polyacrylate hydrolysed acrylonitrile grafted starch, a starch polyacrylate or an isobutylene maleic anhydride copolymer.

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7. A superabsorbent material as claimed in claim 6 wherein the base polymer is a starch polyacrylate or a cross-linked polyacrylate.

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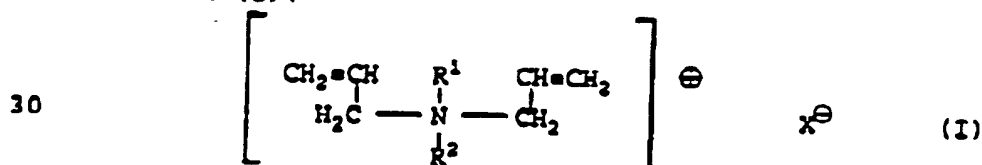
8. A superabsorbent material as claimed in any of claims 1 to 7 wherein the functional groups of the cationic superabsorbent are primary, secondary or tertiary amine groups or quaternary ammonium groups, preferably quaternary ammonium groups.

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9. A superabsorbent material as claimed in claim 8 wherein the functional groups are attached to a polysaccharide base polymer.

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10. A superabsorbent material as claimed in claim 8 wherein the functional groups are attached to a polymer of units of formula (I):



wherein R<sup>1</sup> and R<sup>2</sup> are each independently an optionally substituted saturated hydrocarbon group or aryl group.

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11. A superabsorbent material as claimed in claim 10 wherein the saturated hydrocarbon group or the aryl group may be substituted by one or more suitable substituents selected from carboxyl, ester ( $-\text{CO}_2\text{R}$ ), hydroxyl, ether ( $-\text{O}-\text{R}$ ), sulphate, sulphonate, primary, secondary or tertiary amines or quaternary ammonium groups.
12. A superabsorbent material as claimed in claim 10 or 11 wherein the groups  $\text{R}^1$  and  $\text{R}^2$  and the R groups in the ester and ether substituents have from 1 to 20 carbon atoms, more preferably from 1 to 6 carbon atoms.
13. A superabsorbent material as claimed in claim 12 wherein the  $\text{R}^1$ ,  $\text{R}^2$  and R groups are each methyl.
14. A superabsorbent material as claimed in any of claims 10 to 13 wherein X is a halide, nitrate, phosphate, nitrite, carbonate, bicarbonate, borate, sulphate or a carboxylate anion.
15. A superabsorbent material as claimed in claim 14 wherein X is a chloride or hydroxide anion.
16. A superabsorbent material as claimed in any of claims 10 to 15 wherein the cationic superabsorbent is a polymer of units of dimethyl diallyl ammonium chloride or dimethyl diallyl ammonium hydroxide.
17. A superabsorbent material as claimed in claim 16 wherein the monomer is dimethyl diallyl ammonium chloride.
18. A superabsorbent material as claimed in any of claims 2, 8 or 9 wherein the cationic superabsorbent is a polysaccharide superabsorbent obtained by reacting a fibrous polysaccharide with an excess of a quaternary ammonium compound containing at least one group capable of reacting with polysaccharide hydroxyl groups and having a degree of

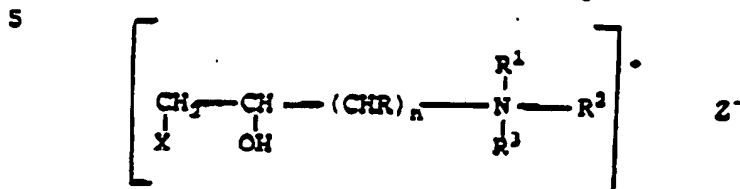
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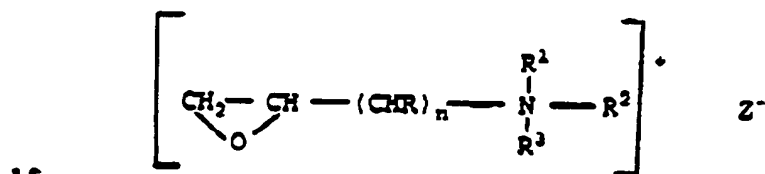
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substitution of 0.5 to 1.1.

19. A superabsorbent material as claimed in claim 18 where the ammonium compound has the general formula

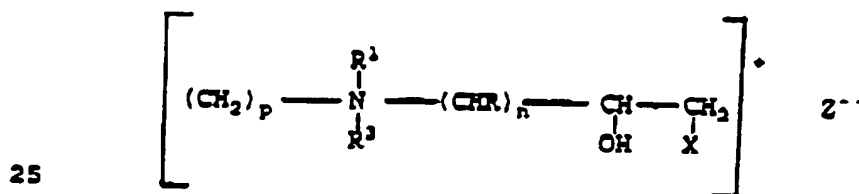


10 or



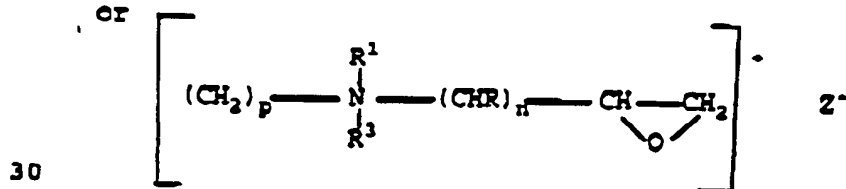
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where n is an integer from 1 to 16; X is halogen; Z is anion such as halide or hydroxyl; and R, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, which may be the same or different, are each hydrogen, alkyl, hydroxyalkyl, alkenyl or aryl and R<sup>2</sup> may additionally represent a residue of formula



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or



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where p is an integer from 2 to 10 and n, R, R<sup>1</sup>, R<sup>3</sup>, X and have the meanings already defined.

20. A superabsorbent material as claimed in any of claim 1, 2, 8 or 9 wherein the cationic superabsorbent is cationic polysaccharide having superabsorbent characteristics the polysaccharide being substituted by quaternary ammonium

groups and having as ds of at least 0.5 and the polysaccharide being cross-linked to a sufficient extent that it remains insoluble in water.

- 5 21. A superabsorbent material as claimed in any of claims 1, 2, 8 or 9 wherein the cationic superabsorbent is a water-swellaable, water-insoluble polymer comprising units derived from a diallylic quaternary ammonium salt monomer, cross-linked by a suitable polyfunctional vinyl compound,
- 10 characterised in that the polymer has been produced by cationic polymerisation in an aqueous phase using a free radical catalyst.
22. A superabsorbent material as claimed in any of claims 15 1 to 21 wherein the ratio of anionic and cationic superabsorbents is in the range 2:1 to 1:5 based on monomer units, more preferably 2:1 to 1:2.
- 20 23. Use of the superabsorbent as claimed in any of claims 1 to 22 for the absorbtion of electrolyte containing aqueous liquids.
24. Use as claimed in claim 23 wherein the electrolyte containing aqueous liquid is menses or urine.
- 25 25. Use as claimed in claims 23 or 24 wherein the superabsorbent is contained in catamenials or diapers.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/15139

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 20/00, 20/22, 20/26; A61F 13/15, 13/20

US CL : 502/400, 401, 402; 604/368, 369

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/400, 401, 402; 604/368, 369; 521/134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, STN

search terms: Procter &amp; Gamble, anionic superabsorb?, cationic superabsorb?, superabsorb?

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,818,698, (WONG) 04 April 1989, col. 2, lines 8-42, col. 3, lines 10-66	1-5
X	us, a. 5,286,827 (AHMED) 15 February 1994, col. 2, lines 33- 66	1-5
X	US, A, 5,354,808 (HSIEH) 11 October 1994, col. 2, lines 29-66	1-5

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document published on or after the international filing date

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

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later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\*

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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document member of the same patent family

Date of the actual completion of the international search

23 FEBRUARY 1996

Date of mailing of the international search report

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